Article

Insights into biogeochemical cycle of mercury, contamination sources and its detoxification techniques. A sustainable approach towards biological remediation.

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ABSTRACT: Mercury (Hg), the environmental toxicant is present in the soil, water, and air as it is substantially distributed throughout the environment. Being extremely toxic even at low concentration, its remediation is utterly important. Therefore, it is necessary to detoxify the contaminant within the acceptable limits before threatening the environment. Although various conventional methods are used, irrespective of being costly, producing intermediate by-product. Biological methods are eco-friendly, clean, greener and safer for the remediation of heavy metals corresponding to the conventional remediation due to their economic and high tech constraints. Bioremediation is now being used for the Hg (II) removal, which involve

Methods:

CMercury (Hg), the most fascinating, rare and potent neurotoxic heavy metal along with distinctive, singular properties like a liquid at room temperature distinguishes it from other elements, belongs to d-group elements. It is nonessential, highly toxic and persistent pollutant that is globally distributed due to its strong persistence and bioaccumulative nature in the environment. Mercury has a high vapor pressure and low solubility, results in freely departure into the atmosphere. Also, Hg is a non-biodegradable element and hence persistent more years in the atmosphere. Now these days the climax of mercury is ascending due to post-industrial activities like the combustion of coal, fossil fuel and petroleum, the operation of mercurial fungicides in farming, paper manufacturing industry, mercury catalysts used in industries, Chlor-alkali plants (Zhu et al. 2018), gold mining (Dranguet et al. 2017), manufacturing of non- ferrous metals, remission from previously deposited mercury on various surface environments like terrestrial region, and cement production leads to a significant increase in global mercury pollution. While the other major factors of mercury pollution are natural sources like hydrological cycle, soil erosion, geothermal activities, and wildfires. Notably, the Mercury released by volcanic sources and burning of coal is an estimated global total of 60,000 kg and 3,000 tons of mercury per year and that is same as the amount released by all the industrial activities. In India, the amount of Hg in coal differs from one place to another according to the physiological characteristics of soil and the average concentration of Hg is 0.3 mg/kg in coal (BHEL 2004). The different forms of mercury are toxic at different levels, among all organic mercury (methyl mercury) is highly toxic (Gray et al. 2015) while the other naturally occurring compounds like mercury sulfide also known as cinnabar is non-toxic. Furthermore, methylmercury was responsible behind the Mina Mata disease in Japan (1952). During the Minamata disaster, industrial wastewater contaminated with methyl mercury was continuously discharged into the bay, which affected the aquatic life followed by human life and another case was held in Iraq (1971) where organo mercury fungicides were used in grains treatment which further consumed by humans, huge population was disturbed by these accidents (Ariya et al. 2015).

biosorption and biaccumulation mechanism or both, also mercuric ion reductase, expolysasscaharide play significant role in detoxification of mercury by acting a potential instrument for the remediation of heavy metals. In this review paper, we shed light on problems caused by mercury pollution, mercury cycle and its global scenario and detoxification approaches by biological class and the result found in the literature.

KEYWORDS : Mercury Bioremediation . Biosorption . Biosorbent . Bioaccumulation . Mercury reductase enzyme . Exopolysaccharides . Phytoremediation

a mercury compound into the environment. Anthropogenic activities, fossil fuel combustion, and atmospheric circulation have enhanced 3 to 10 times Hg in soil and sediments. In 2005, the global Hg emission was reported to be 3000 tons. Moreover, 800 t Hg per year alone released by the burning of fossil fuel and become the superior anthropogenic source of Hg in the atmosphere (Kowalczyk et al. 2016). Being recalcitrant in nature, the removal of Hg is quite difficult and through bioaccumulation, it transfers to the food chain and causes a threat to the human being. As mercury is easily absorbed by the alimentary tracts, it penetrates into the placenta, with the passage of the blood-brain barrier, it disrupts the function of the membrane, protein compounds, nucleic acids, and other enzymes. Heavy metal does not degrade easily like organic pollutants (Barker et al. 2002). Because of having versatile nature and the best conductor of electricity, it is also used in various applications like a thermometer, thermostats, catalysts, electrode materials, electrical switches, reflective liquid in liquid mirror telescope, medicine (dental amalgam), fluorescent light bulbs and ballast for submarines (Gonzalez et al. 2017). The immense increase in the level of mercury in the terrestrial as well as aquatic ecosystem decreases the plant yield and also disturbs the stability of the food web (Hindersah et al. 2018). There are 3 different categories of heavy metals to which we should show concern about, primarily the heavy metals like Hg, Cd, As, Sn, Pb, Co, Cu, Ni, Mn, Fe, etc., radionuclides like Ra, U, Th, Am etc., and the adored metals like Ag, Ru, Pt, Au, Pd etc. Among all mercury, cadmium, and lead is regarded as 'toxic trio' and have no biological importance, also considered as highly toxic and threatening.

Distribution of mercury in the environment

Natural occurrence and chemistry of mercury: Mercury is commonly known as Quicksilver and was formerly named as hydrargyrum. It is silver-white liquid metal belongs to the D group element with extraordinary properties like a liquid at room temperature other than bromine. It exists in elemental, organic and inorganic form, in which organic mercury is highly toxic (methylmercury). It is used in various scientific research applications and in amalgam for dental restoration in some locales.

Kannan et al. (2005) reported that India alone discharged 300 t/annum of

The Mercury cycle: During the biogeochemical cycle of mercury, it endures many physical and chemical transformations and circulated into the atmosphere in Fig. 1. There are two cycles is involved in the distribution and

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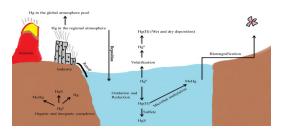


This open-access article is distributed under the terms of the Creative Commons Attribution Non-Commercial License (CC BY-NC) (http:// creativecommons.org/licenses/by-nc/4.0/), which permits reuse, distribution and reproduction of the article, provided that the original work is properly cited and the reuse is restricted to noncommercial purposes. For commercial reuse, contact reprints@pulsus.com transportation of mercury cycle, i.e., global and local. These cycles involve in the atmospheric circulation of elemental mercury and methylation of inorganic mercury from contaminated environment (Boening 2000). The mercury cycle in the environment continues until it gets deposited into the reservoirs like deep-ocean sediments and this cycle in the environment is circulated by biological and geological processes. The concentration of mercury in the surface of the earth's crust varies and found 21 ppb in the lower crust to 56 ppb upper crust in different organic, inorganic and elemental form. Generally, in nature, mercury occurs in 3 valence states, i.e., Hg0 (zero oxidation state , metallic mercury,) Hg2+ (inorganic mercury, mercuric mercury), and Hg22+ (mercury mercury) and these states of mercury balance stability among themselves by the processes of chemical dismutation (Robinson and Tuovinen 1984):

Hg22+ 4Hg0 + Hg2+

Besides elemental form(Hg0), the inorganic and organic form (monomethyl mercury) of mercury is found in soil, water, sediments, and biota but dimethylmercury is only organic form of mercury found in very less concentration in marine ecosystem (Zhu et al. 2018). The mercury toxicity in an aquatic ecosystem is affected by its salinity, dissolved oxygen, temperature, and water hardness. Elemental mercury is the predominant species, with a residence time of 0.5 to 2 years in the atmosphere due to high solubility and chemical inertness in the water while mercuric mercury is reactive gaseous mercury, highly water-soluble, less volatile than elemental mercury with a residence time of days in the atmosphere (Kim et al. 2012). The natural and anthropogenic sources of global mercury discharge into the atmosphere is mercury vapor (Hg0) and this mercury vapor as a result of its interaction with ozone in the presence of water further photo-oxidized to ionic mercury. The gaseous elemental form of mercury is easily dispersed into the atmosphere. However, inorganic mercury reaches to the surface of the earth through rain precipitation where micro-organism present in the aquatic as well as soil ecosystem converts it in different oxidation form of mercury. The elemental mercury has the ability to vaporize easily into the air, so new mercury starts once elemental mercury reaches into the air (Driscoll et al. 2013). Hg2+ plays a fundamental role in the biogeochemical cycle of mercury and toxicology of living things as it is a resultant (product) of the metabolism of vapor Hg and other organic compounds of Hg. Methylmercury is highly toxic among all compounds of mercury, if methylmercury is formed, it gets bio accumulated and translocated in the food chain. As a result, the bio magnification of the organic form of methylmercury causes the predator to have a higher mercury concentration (Dash et al. 2014).

By methylation from inorganic to organic form, several bacteria or fungi transforms the available mercury in the environment (Hg2+) and form a more potent toxic compound than its precursor, mainly sulfur reducing bacteria, iron reducing and methanogenic bacteria are capable of Hg methylation in comparison to other microorganisms. For the transformation of Hg species, sulfur cycle plays an important role as mercury has a high affinity towards sulfur-containing compounds and proteins such as glutathione and metallothionein (Ravichandra 2004).



Different form of mercury, their toxicity and persistence in nature

Elemental mercury (Hg0) and Mercuric ion (II) are a quite common form of mercury present in the atmosphere, whereas mercurous ion (I) or Hg22+ is rarely found (Mahbub et al. 2015). However, Hg (II) and methylmercury also exist in dissolved, colloidal as well as suspended form in water. The High solubility of mercury in an aqueous phase and easy conversion into gaseous phase is the unique properties that clarify the efficiency of mercury to shift in the distinct ecosystem and endure for a long time in the atmosphere, which later gets deposited in the soil or water bodies (Yang et al.2008). As, Hg vapor can exist as a nation in an oxidation state of 0, 1+ (mercurous) or 2+ (mercuric), it plays a pivotal role in the global mercury cycle (Boening 2000).

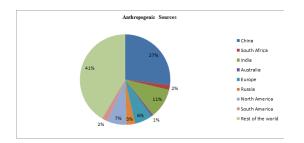
Mercuric chloride (II) as being water soluble is the most potent toxic form of mercury among all forms (Azevedo and Rodriguez 2012). According to "hard and soft acid-base" rule, mercury show intense affinity towards thiol groups and being a soft metal, it forms thiosulphate complexes and characterizes as "B" metal cation (Kim et al. 2012). The thiols compound like mercury thiosulphate complexes increases the leaching of mercury in soil by dissolving the non-mobile phase of mercury and enhance Hg bioavailability in the soil as well as plant uptake. It has been reported that organic form of mercury is much more toxic than an inorganic form of mercury for all aquatic as well as non-aquatic species because an organic form of mercury has the ability to accumulate in the different trophic levels and also have an affinity for sulfhydryl groups present in the proteins. Further, mercury found in aquatic environments in forms like Hg (II) and Hg (0) while in fresh water, it forms more complexes and form compound such as Hg (OH)2, Hg0HCl, and HgCl2 and in seawater it forms complexes HgCl+, HgCl2, HgCl3l, and HgCl421, besides if sulfide is present then it also form mercury sulfide complexes also. However, Hg forms the strong bond with dissolved organic matter (DOM) so that it can form complex easily with dissolved organic matter specifically with thiols groups (Jiang et al. 2018).

The toxicity spectrum of mercury depends on the chemical form in which it is available in the environment: elemental (metallic), organic or inorganic (Kumari 2011). The toxicity of metallic mercury is relatively low as compared to other mercury compound (inorganic and organic) because of their solubility. Metallic mercury has low solubility than other oxidized forms of mercury. The catalase and peroxidase enzymes in vivo condition can convert metallic mercury into oxidized and highly toxic form (Zalups et al. 1996). Bioaccumulation and bio magnifications properties of these compounds, especially methyl mercury make it most perilous for the food chain of human beings as well as wildlife. The physical and chemical parameters of atmospheric species of mercury are described in Table 1.

Compounds	Elemental mercury	Mercuric chloride	Mercurous chiloride	Methyl mercurio chloride	Dimethyl mercury	Mercury(II) axide	Mercury sulphide	Methyl mercury
Structure	a kene ke ana.		$\mathbb{M}_{\mathbb{S}}=O$	Hg=5	н _я СН			
Melecular formula	Hg"	HgCl	Hg:Cl:	CI CI	CH.HgCl	HgO	HgS	CH-Hg
Molar mass (gimel)	200.59	271.52	472.09	251.07	230.662	216.59	232.66	215.62
Oxidation state	0	+2	+1	+2	+2	0	0,-2	NA
Meltingpoint (+C)	-38.8	277	302	270	-43	500 (decomposition)	584 (decomposition)	137
Water solubility(gL*)	49.6×10°(20)	66 (20 C)	2.0×10'g1 at 25'C	0.100 g1 at 21 °C	1g1at 21°C	0.053(25°C)	2+10-**(25C)	NA
Boiling point (+C)	356.7	303	384	NA	93	NA	NA	NA
Vapor pressure (Pa)	0.18	0.009	NA	0.083	NA	9.2+10**	NA	0.9
Density (gicm')	13.534	5.43	7.15	4.06	2.96	11.14	8.10	NA
Physical state	Silver colored Jiquid	White crystalline solid	White crystalline solid	NA	NA	yellow or red crystalline solid	Black or red crystalline solid	NA

Global hotspot of mercury

In Asian countries, the emission of mercury has been described to be like China (604.7 mg), Japan (143.5 mg), India (149.9 mg) and Kazakhstan (43.4 mg) (Dash et al. 2012). Among all these countries, China is the principal country with maximal Hg emissions from the industrial exercises. China alone supply about 28% of the universal mercury emission. In Asia, enhanced mercury pollution may undoubtedly affect the mercury deposition in North America due to the long-range transport (Li et al. 2009). As per authoritative reports, Russia facilitates about 70 mg/yr of mercury by all the anthropogenic activities. In Australia, the emission rate of mercury from man-made activities was found to be 16.6 mg/yr. However, this estimate is much larger as per the report provided by the National Pollution Inventory (1.1 mg/yr). Trade and environment database (TED) reported that Brazil release mercury about 200 mg/yr into the atmosphere (Pirrone et al. 2010). According to the UNEP (2008) report, in Europe the overall release of mercury is 145.2 mg/yr, in which the principal addition of mercury is from static combustion sources by 52%, while 38% contribution is from Chloralkali plant, cement industry and ferrous and nonferrous metals and the last 10% arrives from other mercury uses and waste incineration (Dash et al. 2012). In case of India, the major contributor of mercury emission is coal combustion with 52% and waste disposal by 32% and the other sources are iron and steel industry, chloralkali plant, non-ferrous metallurgical plants, cement industry, and other minor sources. Furthermore, it was observed that the emission rate of mercury has decreased from 321 mg in 2000 to 241 mg in 2004 (Pirrone et al. 2010). The emission rate by all the developed countries is shown in Fig. 2.



In case of India, the outskirt of Uttar Pradesh, Singrauli region is surrounded by huge coal mine and super thermal power plants (STTP) namely Singrauli STPP, Vindhyayachal SSTP, Rihand STTP, Anpara A, and B STTP, Renusagar STTP. The power generation capacity of singrauli is 9.5% to that of total production in India and Singrauli only contribute about 16.85% of entire Hg pollution by electricity generation. The Hg concentration was found to be higher than that of 5 μ g/ml for 66.3% of the total sampled population as per data are given by the Industrial toxicology research Centre, Lucknow. The concentration of Hg was found around 0.182 mg/l in that area (Yadav et al. 2017). Thoothukudi is also named as Tuticorin and "Pearl City" is located in the Tamil Nadu and also known as one of the hubs of coal and thermal power plant. The Tuticorin district is enclosed by the Gulf of Mannar and Southeast Asia. In this region, there are 5 thermal power plants TPPs, by using 17-18 Gg of coal per day the electricity production is about 210MW. In the respirable suspended particulate matter (PM10) the concentration of Hg was found to be 0.02- 0.01 µg/m3 (Kumari et al. 2009). In Tamil Nadu, Kodai Lake, Kodaikanal is a hill resort and a famous tourist place too. This place was found to Hg-contaminated from the residue waste by thermometer manufacturing industries. The total Hg and methylmercury were found to be 356-465 ng/l and 50 ng/l in water samples, whereas in the sediments the concentration of Hg was about 276-350 mg/kg. In the samples of fish, the reported concentration of Hg was about 120-290 µg/ kg. (Karunasagar et al. 2006). Also in Orissa, the area near the Rourkela steel plant is mainly affected by mercury pollution. The steel industry and other medium industries like fertilizers, Chlor- alkali plants, cement, heavy machinery, factories, mining, explosives, distillation, chemicals, and sponge iron mills etc. (Panda et al. 1990).

Catastrophic effect of mercury

Effect of Hg in human beings: The compound of mercury is extremely toxic for neonate especially in the form of methylmercury and this form of mercury is liable to inhibit the function of microtubule and mitochondrial, lipid peroxidation and deposition of neurotoxic molecules such as glutamate, aspartate and serotonin. Being a neurotoxin and teratogenic, it is easily absorbed by the gastrointestinal tract and through the bloodstream spread into the whole body (Vacchina et al. 2017). Excessive intake of mercury can cause health impacts and damage like the immune system, cardiovascular system and nervous system (Huang Ying et al. 2017). It can also damage organs like the heart, brain, lungs, and kidney (Raj et al. 2017). The major spot organ for the accumulation of inorganic mercury is kidney where is gets deposited and express toxicity (Zalups et al. 2018). The excess exposure to mercury can also lead to mental retardation, cognitive impairment, and developmental delay. On the other hand, Methyl mercury has the ability to cross the placental membrane and enter into the blood-brain barrier. In some studies, it has been reported that high concentration of methylmercury was found in the fetus than in mother result in neurotoxicity i.e., severe mental and physical developmental retardation, extreme fetal abnormalities. microcephaly, blindness (Kim et al. 2012). Other diseases like Parkinson's, Alzheimer's disease, sclerosis, and Autism spectrum disorder are also expedited by some heavy metals exposure (Bjorklund et al. 2017).

Effect of Hg in plants: The functional alteration created by mercury in plants causes a metabolic and physiological disorder. The inorganic mercury for root uptake in the soil is mostly available when it is bound with fulvic acid. Once mercury enters into the plant via root, then the intracellular Hg binds to phosphate, *ISH* group and other active groups in ADP and ATP. On the other hand, the mitochondrial activity alters cell membrane permeability, provoke the production of ROS, which leads to the substitution of essential cations and disrupts the bio membrane lipids and cellular metabolism in

plants, also affect photosynthesis, water plant balance and inhibit growth (Messer et al. 2005; Lutts 2014), constrained the pigment synthesis, transform the permeability of the membrane, decreased the weight and size of shoot and root (Sharma et al. 2018).

Detoxification of mercury

Today, the major issue or man's considerable threat is to tackle with heavy metal pollution, which has been increasing and damage ecosystem directly or indirectly. In contrast to organic pollutant which is easily degradable, heavy metal pollution is persistent in nature and accumulates in the soil and sediments, as heavy metals do not degrade but it can convert or transform from higher to lower toxic state. Overall list of conventional methods (physical and chemical) and biological methods for Hg remediation is given in Table 2.

Physical methods	Chemicalmethods	Biological methods
Adsorption	Addition of electron	With the help of bacteria, fungi, algae, plants an
Vitrification	donors likes:	their biomass etc.
Membrane filtration	Hydrogen sulfide (H2S)	The major mechanisms involved:
Reverse osmosis	Sodium dithionite	Biosorption
Granular activated carbon	(Na2S2O4)	Biotransformation
Electrokinetics	Sodium metabisulfite	Bioaccumulation
Soil flushing	(NaHSO1)	Biomineralization
Soil washing and	Calcium metabisulfite	Extracellular precipitation
Separation	(CaHSO ₃)	
Electrodialysis	Calcium polysulfide	
	(CaSt)	
	Ferrous sulfate (FeSO4)	
	Photocatalysis	
	Stalilisation/solidification	
	Precipitation	
	Ion exchange	

There are many methods like physical, chemical and biological methods which have been used in the past few decades for the remediation of contaminated soil and water. For the treatment of mercury in soil and other wastes, treatment like solidification or stabilization, soil washing, vitrification, and thermal treatment have been applied while in case of contaminated water, the method of precipitation or coprecipitation, adsorption, membrane filtration is being employed (Wang et al. 2012), but the bioremediation is a thoroughly common phenomenon for the contaminated soil and water treatment (De et al. 2008). With the help of bioremediation and its application, the treatment becomes quite cheaper and effective in contrast to that of physical and chemical methods (Dash et al. 2012). A physical and chemical treatment has become costly as well as poses handful damaging effects on the environment while bioremediation is social, economic and environmentally friendly. The only disadvantage of the bioremediation is that after remediation, the biomass collected is toxic, if not being handled with the proper management it can find its way to somehow get back into the environment.

Physical and chemical method of mercury detoxification: Now these days the increasing heavy metal pollution is a big reason in environmental destruction and also the greatest challenge to human to cope up with heavy metal pollution. The heavy metal pollution is different from other organic pollution because it cannot degrade easily as that of organic pollution. Heavy metals have the ability to accumulate in the living tissue and add into it. However, the remediation of mercury is possible through methods like physical, chemical and biological.

The physical method of remediation techniques like adsorption, photo catalysis, granular activated carbon, membrane filtration, electro dialysis method, capping soil washing and in situ vitrification have been operating to remediate mercury-contaminated soils (Ma et al. 2014; Wang et al 2012). The physical remediation method can be performed either in in-situ or ex-situ. In this method, separation of contaminants from soil is done by the volume reduction process, which reduces the original volume of a contaminant followed by transfer the residual contaminated part to another medium for further processing and treatment.

In case of chemical methods, the utilization of chemicals makes changes in the properties of the contaminant and minimizes the ecological threat by diminishing the pollutants accumulated in the soil or aquatic system by transforming the state of contaminants. In chemical treatment various chemicals are being used for the remediation of contaminated soil and water like Calcium metabisulfite (CaHSO3), Ferrous sulfate (FeSO4) Hydrogen sulfide (H2S), barium sulfate, sulfur dioxide, Sodium dithionite (Na2S2O4), ferrous sulfate, sodium metabisulfite, sodium sulfite lime, Calcium polysulfide (CaS5), and limestone for reduction (Jobby et al. 2018). The chemical destruction process used in chemical remediation involves oxidation to carbon dioxide by using chemical oxidants like hydrogen peroxide (H2O2) or by the transformation reactions comprises of dechlorination with the help of alkaline reagents and chemical or ultraviolet (UV) reduction (Fox 1996). The main disadvantage of physical and chemical remediation is the production of bulk mass of toxic wastes, it is costly and energy consumption is high as well as need huge scale application. These disadvantages make physical-chemical remediation less efficient than biological remediation, as it does not require such high-tech technology.

Biological methods: The use of microorganisms (bacteria, fungi, algae, yeast) for the remediation of contaminated soil, air and water is known as bioremediation (Gavrilescu et al. 2009). Both living things and non-living materials are involved in the bioremediation as a biological agent. The temperature, structure, pH, moisture content, quality of pollutants, microbial community of the affected sites and nutritional state are the major factors which influence the success of bioremediation. Though it is a very economical method of remediation as it does not cause any catastrophic effect on the environment.

In bioremediation, the major mechanism which works efficaciously in remediation of the contaminated soil and aquatic system are biotransformation, biosorption, biomineralization, biovolatilization and bioaccumulation by the microorganisms (bacteria, fungi, and algae) and phytoremediation is carried out by using plants in the contaminated environment. In all these methods, biosorption and bioaccumulation is most promising and convenient method as it has low operation cost and proved very efficient for the remediation of contaminated soil and aquatic system.

Biosorption

Biosorption can be defined as a metabolically mediated passive process or physicochemical pathways for metal sequestration from the contaminated environment with the help of dead or inactive cells or biomaterials. Precipitation, ion exchange and complexion are the common mechanisms of biosorption of heavy metals and their concomitant occurrence is due to the presence of several functions or reactive groups or biomolecules on bio Sorbent (Hansda et al. 2016). Usually, microorganisms have the skill to remove the heavy metals from the contaminated soil and water. Microorganism uses heavy metal/pollutant as their source of food or nutrition for survival due to having the adsorptive and accumulative capability. Biosorption is sometimes very similar to the ion exchange method or adsorption, the only difference in between these is sorbent nature.

Mechanism of biosorption: The mechanism of biosorption is mainly based on the cell metabolism of microbes which further categorized as metabolism dependent or metabolic independent, also categorized as extracellular or intracellular accumulation or precipitation and cell surface sorption of biosorbent depends on the metal removal location in the solution. It is a simple physiochemical phenomenon in which pollutants adhere to the cell wall of biosorbent. Metabolically inactive cells or dead cells constitute the active biomass for biosorption. In this process, the paracrystalline S-layer protein in the bacterial cell made up of glycoprotein and protein subunits helps in the adhesion of heavy metals to the surface of the cell either of any one process like ion exchange, physical adsorption, van der Waals forces, and inorganic precipitation. Carboxylate, phosphate, hydroxyl, an amino group, and sulfate are some functional groups which help with the metal binding to the surface of the cell, secreted by the component of bacterial cell walls like polysaccharides, lipids, and protein (Veglio and Beolchini 1996). As biosorption is metabolism independent, so it usually reversible and the binding of metals occurs very fast likely in 1 minute (Kadukova and Vircikova 2015). Some microalgae (Ulva Lactuca, Gastrotheca gracilis and Fucus vesiculosus) have also been reported to the good source of bio Sorbents (Henriques et al. 2015). Khoramzadeh et al. 2013 in their study reported that sugarcane bagasse is the best and cheap source of sorbent as made up of cellulose, lignin and pentosan and existence of adsorptive sites such as carboxylic, hydroxyl, amine, and carbonyl groups make it economical biosorbent. Also, the castor tree (Ricinus communis L.) proved as an excellent sorbent which can remove methylmercury and mercury (II) from aqueous media (Al Rmalli et al. 2008).

Biosorbent: Biosorbent is renewable biological materials acts as potential agent for the heavy metal uptake. It act as natural ion-exchange materials which consist of weak acidic and basic groups, the chelation process being unspecific. The origin, availability, and cost-effectiveness play an important role during bio sorbent selection (Hansha et al. 2016). The biosorbent have metal sequestration ability which can decrease the concentration of heavy metals from ppb to ppm level. The major reactive group found

in the bio sorbent for the binding and sequestration of heavy metal is an amine, carboxylic, phosphate, sulfhydryl. These reactive groups help in efficient metal adsorption. The nature of some bio sorbent is specific for a few heavy metals while some are common to all heavy metals without any specific activity and the selection of bio sorbent is achieved either by environment directly or by advisable modification methods. It has been observed that many laboratories used naturally or easily available biosorbent for adsorption while some laboratory used modified biosorbent which has the ability of effective sequestration of metals and other contaminants. Diverse biological creatures (bacteria, algae, fungi,) and their sub-products (alginate, Chitosan) shows enhanced metal adsorption capacities (Plaza et al. 2011). Besides live biomass, dead biomass are also used as a bio Sorbent for effective sequestration. The preference for dead biomass is higher than live biomass because dead biomass do not require any further condition for growth and survival as it is simpler to handle than living biomass while the live biomass requires maintenance of living cell condition and culture growth media (Volesky 2007; Malik 2004). The efficiency and performance of dead biomass can be modified and enhanced by some activation methods work which later on works effectively with more adsorption potential (Tuzen and Sari 2010).

On the other hand, bioaccumulation is a process that involves the deposition or accumulation of heavy metals inside the biological components (Jocab et al. 2018). Another important method which is helpful in the conversion of inorganic to elemental mercury is biotransformation method. Fe2+, fumic and humic acid are the major reductants present in soil, which help in the transformation of mercury. The reduction and volatilization of mercury in the soil are enhanced by temperature and solar radiation while in the dry ecosystem, increased soil moisture promotes volatilization of mercury (Engle et al. 2005). In this, the higher toxic form of inorganic mercury is converted into a less toxic element form, i.e.

Hg2+ Hg0 (Mirzaei et al. 2008).

The high vapor pressure and low aqueous solubility are responsible for the transformation of Hg2+ to Hg0. However the major problem in bioremediation and phytoremediation is the production a huge amount of mercury-loaded biomass and the dumping, disposable and incineration of such huge biomass are problematic.

Bioaccumulation: It is the complex and non-equilibrium process resemble sometimes to that of biosorption, in which heavy metal removal is done by living cells by mean of accumulation of pollutants inside the biosorbent cells while in biosorption the removal of heavy metal is done by metabolically inactive or dead biomaterials. Also, bioaccumulation is known as active biosorption or adverse to passive bioadsorption (Kadukova and Vircikova 2015) and more complex process than that of biosorption (Chojnacka 2010). This process consists of two steps, first one metabolism independent process also knows as extracellular binding is relatively faster than second metabolism dependent process known as intracellular binding. The metabolism independent process is initial rapid accumulation step responsible for metal ion binding to the surface of the cell of bio Sorbent while metabolic dependent process accumulates a huge amount of metal ions and relatively slower than first process (Aksu and Donmez 2005). Though it utilizes the living cell and metabolic activity for metal removal so that the physical parameters like temperature and light sources might affect the metabolic functions. In this process, the metallic ion uptake is done by intracellular compounds via ATP-driven active transport or via intracellular precipitation (by sullde or phosphate ions discharge) or by methylation, demethylation, oxidation and reduction mechanism (Hansda et al. 2016). Also the synthesis of thiol rich, low molecular weight metallothioneins protein supports the process of bioaccumulation which helps in the binding of metal ions. Species isolated from the contaminated region with heavy metals helps in potential bioaccumulation. In literature, it is found that in comparison to algae and fungi, bacteria can accumulate heavy metal at the diverse atmospheric and external condition. Deng et al. (2012) is his study proved that marine strains resistant to mercury have the ability to accumulate Hg in its cell and accumulate about 70% Hg2+ on the surface of the bacterial cell at pH 4-10. The carboxyl group present in the surface of bacteria was responsible in Hg2+ binding. In another case, Sinha et al. (2013) isolated five bacterial strains and the genera were Enterobacter, Bacillus, and Pseudomonas. Among these genera, Enterobacter sp. were able to accumulate mercury in its cell and help in 99% mercury removal at different pH condition and proved as effective for remediation of mercury.

Both biosorption and bioaccumulation mechanism has several advantages over conventional methods as they have low cost, minimize the residual product discharged after treatment, no nutrient requisites and highly effective in dilute effluent detoxification.

Detoxification by bacteria:

The Mechanism of metal resistance in bacteria includes precipitation of metals as carbonate, phosphate or sulfides; volatilization via methylation and demethylation; physical inclusion of electronegative substance in membrane and extracellular polymeric substance; energy-dependent efflux system and intracellular sequestration with low molecular weight, cysteine-rich protein (De et al. 2008). The remediation of mercury with bacteria is fast, less energy consuming and economic process. In some case, microbial surfactant has additionally been reported to be utilizable in bioremediation of mercury (Sorkhoh et al. 2010). Both gram positive and negative bacteria have revealed the skill of mercury resistant bacteria to remediate the contaminated environment by the process like biosorption, biotransformation, bioaccumulation, and biovolatilization (Jobby et al. 2018). Because of having high surface to volume ratio and active chemisorption sites as teichoic acids in the bacterial cell wall, makes bacteria a potential biosobent (Vijayaraghavan and Yun 2008). Among the entire microorganism, bacteria consist of special functional groups such as phosphonate, sulfonate, hydroxyl, carboxyl, and amide groups, these groups help in the metal uptake and transformation process. Certain bacteria like bacillus and Pseudomonas because of their high binding affinities towards heavy metals, have been used for the remediation of the contaminated environment (lacob et al. 2018). Many mercury resistant bacteria have been described previously belonging to genera Citrobacter, Pseudomonas, Staphylococcus, Enterobacteriaceae, Proteus, Brevibacterium, Alteromonas, Xanthomonas Aeromonas, Escherichia, Rhodococcus, Klebsiella, and Bacillus are commonly used in bioremediation. For example, Dash et al. (2013) performed an experiment with different strains of mercury - resistant bacteria. The selected strains were Bacillus thuringiensis, Enterobacteriaceae, Bacillus sp., Aeromonas sp., Pseudomonas aeruginosa, Proteus sp., and Xanthomonas sp. Among all these strains, Bacillus thuringiensis showed higher resistance to mercury and the result depicted a fascinating remediation potential of 65.78% - 96.73% of all isolates in the remediation of mercury. Mahbub et al. (2016) evaluated the efficiency of mercury-resistant bacteria isolated from soil of New South Wales, a mercury-contaminated region in Australia. The mercury resistant strain was perceived as Sphingopyxis exist for the Sphingomonadaceae family of the I-Proteobacteria group. The strain was proved efficient in mercury removal by about half of the added inorganic mercury within 6 hours by volatilizing inorganic mercury from the media. In another case, Figueiredo et al. (2014) isolated mercury-resistant bacteria from the sample of two high mercury-polluted areas of the Tagus Estuary (Barreiro and Cala do Norte) and one natural reserve area (Alcochete), in which the bacterial Hg-methylation was performed by Bacillus megaterium, Vibrio fluvialis, and Serratia marcescens that transformed 2 to 8% of whole mercury into methylmercury in 48 hours and most of the mercury resistant bacterial isolates showed Hg2+ reduction and Hg0 volatilization corresponds to 6-50% loss of mercury from the culture media. Saranya et al. (2017) assessed the remediation potential of bacteria isolated from the SIPCOT effluent discharge area. The isolated strain was identified as Vibrio fluvialis with the help of 16S ribosomal RNA gene sequences. The removal ability was checked at different mercury concentration, i.e. 100, 150, 200 and 250 µg/ml and the valuable bioremediation were noticed at 250 µg/ml along with 60% removal of mercury ions. Giovanella et al. (2015) reported 86% of the total mercury removal through the isolation of Pseudomonas sp. B50A strain, the optimum activity of mercuric reductase was in the range of temperature 37-45°C. It was also depicted that Pseudomonas sp. B50A strain could be used in the bioremediation of mercury due to its capability of maintaining 50% of its mercuric reductase enzyme activity in optimum temperature (1-75 °C) and alkaline pH (9). François et al. (2017) examine the mercury resistant bacteria capable of exopolysaccharides secretion, which is a primary indication of the mucoid phenotype. In his study, he reported that the isolated bacteria were capable in the secretion of exopolysaccharides along with mucoid phenotype. The killed bacterial biomass represent the more sequestration ability than that of live bacterial biomass and the effective sequestrations of killed bacterial biomass were 40 to 120 mg mercury per gram in dry weight while live bacteria were sequester 1 to 2 mg mercury per gram in dry weight. Mukkataa et al. (2019) studied the remediation potential of purple nonsulfur Hg resistant bacteria, isolated from the shrimp ponds. The isolated stains grown in different growth condition, i.e. aerobic dark conditions and microaerobic light condition and strains identified as Rhodovulum sulldophilum and Allfella marina. The results demonstrated that a dead cell of all the strains was significantly higher efficiency for removal of mercury than live cells. The highest mercury removal efficiency was 87% - 95% of both the live and dead cells. Few supplementary research experiments of bacterial-mediated removal of mercury are outlined in Table 3.

Sl no.	Name of organism	Isolation site		Mechanismused	Optimum (pH & Temperature)	Percentage remediation	Time	References
1	Brevundimonacsp.	Goldmine		Bioaccumulation	NA & 37°C	64%	NA	Irawati et al. 2012
2	Escherichia coli	Purchased		Volatilization	5-7 & 30°C	93%	18 h	Wang et al. 2018
3	Lyzinibacilluz zp. And Bacilluz zp	Black sand (volcanic area, Southern Iceland)	beach	Biosorption	7 & 28°C	97%	16 h	François et al. 2012
4	Bacillus firmus	Gavkhuni wetland	Iran)	Volatilization	7.5 & 35°C	50%	72 h	Noroozi et al. 2017
5	Sphingomonadaceae	New South Australia	Wales,	Volatilization	6.4 & 25°C	67%	24 h	Mahbub et al. 2016
6	Pseudoxanthomonat Sp	New South Australia	Wales,	Volatilization	6.5 & 25°C	60%	24 h	Mahbub et al.2016
7	Sphingomona	New South Australia	Wales,	Volatilization	6.4 & 25°C	79%	24 h	Mahbub et al. 2017
8	Sphingopyxisalaskansis	Comwallis	Island,	Biotrans formation	NA & 46°C	90%	24 h	Poulain et al. 2006

Role of mercury reductase enzyme regarding Hg removal of bacteria: Interesting, it is found that most of the bacteria have mercury resistance genes which help in the reduction of ionic forms of mercury into a volatile form via well-known mercuric ion reductase, a homodimer, a key protein in mercury volatilization, inducible enzyme, known as merA and the reduction is done with the help of the group of a gene that is present in the operon known as mer operon (Barkay et al. 2003). The mer operon located either in the genomic DNA, transposon Tn501 and Tn21 (Huang et al. 2019), or intron or in the plasmid. MerA serves to convert mercury from highly toxic state, i.e. Hg2+ to relatively less toxic state, i.e Hg0 as well as execute duplication, enzymes distribution and act as a transporter, promoter and regulator for cells (Barkay et al. 2003). Moreover, mer operon also consist of the other functional genes such as merA, merB, merC, merD (regulatory protein), merE, merF, merG, merP (periplasmic scavenging protein), and merT (the inner membrane protein) code for a specific protein and help in the transformation of inorganic to organic mercury (Zheng et al. 2018). The mercury ion reductase is an oxidoreductase enzyme and Flavin adenine dinucleotide (FAD) that play an enormous role in the transformation of mercury from Hg (II) to Hg (0). Due to high vapor pressure of elemental mercury, Hg(II) get easily volatilizes and transforms into Hg (0) and move into the atmosphere which lead the environment mercury free (Bafana et al. 2018). Also, MerA gene commonly found in the bacteria and archaea, these species can survive even at high mercury concentration. MerT and merP acts as enzyme transporter and by transport the thiolated inorganic mercury into the cytoplasm help in the transformation of mercuric reductase while merR acts as regulator of mer operon expression in the Hg resistance system (Freedman et al. 2012). The metabolic function performed by the merA gene is incomplete in the absence of the transporter gene merT, merP and regulatory protein merR. This regulatory protein executes dual job and cooperates in the regulation of mer function as it conducts the transcriptional activation and repressor. The role of merG is to reduce the cellular permeability towards the organomercury speices while merE gene mediates in transportation of Hg2+ and methylmercury by acting as extensive transportor of mercury (Rojas et al. 2011). MerD is another suggested regulatory protein which act either as co-activator or co-repressor in transcriptional activation, also form ternary complex in cooperation with merR and operator or promter to regulate the mer system expression. MerR perform as activator or repressor in the transcriptional activities in state of mercury stress, it act as a transcriptional activator by stimulating the mer genes expression. The Flavin adenine dinucleotide (FAD) as an electron source present in the mercury ion reductase, helps in the reduction of Hg2+ (ionic form) to Hg0 (elemental form) by using an electron donor NADPH.

Mechanism of mer gene mediated detoxification: MerA-NADPH and MerA-FAD compounds performed a central role in the volatilization and subsequent binding of mercury (Dash et al. 2017). Pair of cysteine residues help in charge transfer reaction in detoxification of mercury (Giovanella et al. 2016). Initially mercury bind to the cysteine residual pair at position 17 and 14 on the periplasmic protein MerP, which further transfers the cysteine residue at position 561 and 562 to the cytoplasm or transporter protein, MerT. MerT contain pairs of cysteine residues in the periplasmic side membrane which transfer mercury to the pair of cysteine residues placed to the other cytosolic side. Once mercury bound to the transporter protein MerT at cytosolic side, it directly move to the pair of cysteine residues to the NMerA (amino-terminal domain of MerA) which further deported mercury to the pair of cysteine residues on the NADPH active site for NAD(P) H-dependent transformation of Hg2+ (toxic mercury cation) to Hg0 (inert, less toxic, monotonic, a volatile form of mercury) (Dash et al. 2017; Freedman et al. 2012; Hong et al. 2014; Zheng et al. 2018; Giovanella et al. 2016). Furthermore, the mer determinants are broadly classified as narrow spectrum that are resistant to inorganic mercury and the broad spectrum that are resistant to both organo mercurials (methyl mercury and phenyl mercury) and inorganic mercury salts (Mirsa et al. 1992). However, in the transformation of mercury, mainly two enzymes perform an important role, i.e. mercuric reductase and organo mercurial lyase. The MerA (mercury reductase enzyme) and MerB (organomercury lyase enzymes) gene in a combined way perform the Hg detoxification mechanism (Mahbub et al. 2016). Mercuric reductase helps in the reduction of the watersoluble ionic form of mercury (Hg2+) into insoluble elemental mercury (Hg0) while organo mercurial lyase helps in splitting the carbon-mercury bond of the organo mercuric compounds (Kannan and Krishnamoorthy 2006). The mer based system plays central in development, metal regulation, enzymatic conversion, transport and construction of biological techniques for the control, management and bioremediation of mercury contaminated environment (Giovanella et al. 2016). Few anaerobes like sulfate-reducing and iron-reducing bacteria consist of katG and katE genes lead to the synthesis of hydro peroxidase which further help in the Hg0 enzymatic oxidation. Escherichia coli, Streptomyces, Desulfovibrio desulfuricans, Bacillus, Geothrix fermentans, Cupriavidus metallidurans and Shewanella oneidensis are few bacterial strains which were assisted in Hg0 oxidizing (Huang et al. 2019). In literature, Brim el al. (2000) used Deinococcus geothermalis for the mer based detoxification of radioactive waste treatment, as this species have radiation resistant ability among all known organisms. Rojas et al. (2011) reported that Cupriavidus metallidurans strain showed effective role in mer mediated mercury remediation from the mercury contaminated water . The role, function and location of all the mer gene are described in Table 4.

Genes	Coded protein	Functions	Location
nerA	Mercuric reductase	Hg?" to Hg? transformation	
nerB	Organomercurial lyase	Breakdown of C-Hg+ bond	
merR.	Regulatory protein	Transcriptional activation and repressor	Cytoplasm
nerD	Regulatory protein	Act either as co-activator or co-repressor and regulate the <i>mar</i> system expression	
Tue	Transport protein for mercuric ion	Act as Transporter and help in transformation of mercuric ion	
merC	Transport protein for mercuric ion	Transport of mercuric ion	Inner membrane
merF	Transport protein for mercuric ion	Volatilization of mercuric ion	
merG	Resistance protein	Reduce the cellular permeability towards the organo mercury species or complexes,	
nerP	Periplasmic binding protein	Transportation of mercury ion	Periplasm
nerE	Transporter protein	Mediates in transportation of Hg2+ and methylmercury by acting as extensive transporter of mercury	Inner protein

Exopolysaccharides (EPS) produced by bacteria and its role in mercury detoxification: Exopolysaccharides are an intricate fusion of high molecular weight microbial (prokaryotic and eukaryotic) polysaccharides, also characterized as homopolysaccharides and heteropolysaccharides. Numbers of bacteria have the ability to secrete contrasting type of polysaccharides. Glycoproteins, polysaccharides, humic and uronic acids, protein, nucleic acid, lipids, organic and inorganic compounds are the common EPS secreted by the bacteria. As per literature protein, carbohydrates and metallic ions like Mn, Mg, Fe, and K are the major constituents of EPS. It provides carbon and energy sources as well as provides protection against water deficiency. EPS mainly occurs in two arrangements, namely capsular polysaccharides (tightly bound with cell wall) and ropy EPS (free loose layer of slime). Also, the biofilm of bacteria are generally made up of exopolysaccharides, secreted protein and DNA (Yildiz et al. 2018). In literature, bacteria, such as Desulfovibrio sp., Rhodococcus sp., Pseudomonas sp., Paenibacillus sp., Shewanella sp., have been reported to have high potential in heavy metal removal (Wei et al. 2016). The chemical group secreted by gram positive and gram negative bacteria varies according to their cell wall component and environmental surroundings like teichoic acids, peptidoglycan, extracellular polysaccharides, lipopolysaccharides, extracellular polymeric substance and capsular polysaccharides. These groups provide sites for the chelation of metals and by this is it clear that bacterial polysaccharides can be efficient in heavy metals bio sorption. Exopolysaccharides provide structural strength, support and integrity to membrane and help in antibiotic resistance against the host immune system.

As in literature, biosorption is carried out by inactive or dead biomaterials and it is a cell surface sorption phenomena. Exopolysaccharides facilitate a bio sorption mechanism while detoxification. Also, Exopolysaccharide use three molecular mechanisms: the synthase-dependent pathway; the Wzx/Wzy-dependent flippase pathway and the ATP-binding cassette (ABC) transporter-dependent pathway (Low and hawell 2018). Its support the growth and provide self-defense in case of severe condition such as pH, temperature and starvation state. The anionic composition of exopolysaccharides helps adequately in sequestration of positively charged heavy metal ions by electrostatic attraction in between them at specific sites (Gupta and Diwan, 2017). Eukaryotes like phytoplankton fungi and prokaryotes like eubacteria archaebacterial play an important role in the EPS production. Dextran, a water soluble glucan, was the first commercialized EPS, which is secreted by Leuconostoc Streptococcus and used by different industry for the manufacturing of food products. Ion exchange, the formation of complex, surface precipitation is a major mechanism involved in the EPS binding to the heavy metals, although the binding process of EPS might vary according to structural composition, availability and pores of the binding site of EPS. Heavy metal makes organometallic complexes by forming bonds with amine groups, polysaccharides and phospholipids consist of EPS. The pH helps in the manufacture of organometallic complexes as it balance the cationic or anionic balance on the EPS membrane. The formation of complex is solely based on hydrophilic interaction in between the carboxylic or phosphoric groups of EPS and heavy metals. The hydrophilic interactions guide the heavy metal to adhere to the membrane of EPS. Fraction of EPS and characteristics of heavy metals play pivotal role in EPS adsorption capacity and the adsorption ability of EPS increases with the decreased heavy metals hydration radius, as higher adsorption favors towards lower radius of hydration, also EPS amphiphilic properties play an important part in potential adsorption capacity towards heavy metal.

Application of exopolysaccharides in mercury detoxification: Exopolysaccharides is secreted by the bacteria in the condition of heavy metal stress, which provide protection to microorganism against heavy metal inhibition. The genes which are responsible for EPS synthesis mainly occur in the genome or plasmid in gene clusters. Exopolysaccharides secreted by the bacteria works as a protection barrier against heavy metal stress. Due to low in cost, environmental favorable and sustainable in nature, exopolysaccharides is considered as excellent for heavy metal detoxification in comparison to conventional technologies. Ovetibo et al. (2016) in his study reported that exopolysaccharides secreated by the yeast yarraowia spp. was able to form EPS-Hg complex. Different functional groups like S=O, C=O, -NH, -OH, carboxylate anions, and ester showed distinct affinities for the complexation of Hg2+. By this experiment we can state that the formation of EPS-Hg complexation followed by precipitation is a potential strategy for bio removal of mercury from the mercury contaminated waste water. François et al. (2017) examine the mercury resistant bacteria capable of exopolysaccharides secretion, which is a primary indication of the mucoid phenotype. In his study, he reported that the isolated bacteria were capable in the secretion of exopolysaccharides along with mucoid phenotype. The killed bacterial biomass represent the more sequestration ability than that of live bacterial biomass and the effective sequestrations of killed bacterial biomass were 40 to 120 mg mercury per gram in dry weight while live bacteria were sequester 1 to 2 mg mercury per gram in dry weight. Rasulov et al. (2013) evaluated the removal efficiency of exopolysaccharides secreted by Azotobacter chroococcum. The production of alignate polysaccharides, which have the ability to detoxify the metal contamination, helps in mercury removal by 47.87% at varying pH from the waste water. Kalpana et al. (2018) reported that exopolysaccharides producing Bacillus cereus VK1 bacteria were able to remove and adsorbed about $80.22 \mu g$ Hg2+ in LB broth and 295.53µg Hg2+ in M9 media which was optimized for enhanced adsorption. Baldi et al. (2017) reported that Klebsiella oxytoca strain were capable of exopolysaccharides secretion. 7.5% mercury was absorbed by the extracellular polymeric substance secreted by the Klebsiella oxytoca strain. In this study the N-heterocyclic member of proteins have faster ability to bind with Hg2+ than carboxyl and hydroxyl member of the polysaccharide. Exopolysaccharides also have the flocculation ability for aggregation and attachment of microbial group in case of wastewater treatment (Lee and Chang 2018).

Application of Bio flocculants in heavy metal elimination: Bioflocculants are group of microbes made up of extracellular biopolymer. The main components are lipids, glycolipids, proteins, glycoprotein, nuclei acids and exopolysaccharides. In literature, algae, fungi, bacteria and actinomycetes were reported to be capable of bio flocculants production. Rhodococcus erythropolis, Nocardia amarae, Bacillus licheniformis, Nocardia amarae, and Pacilomyces sp., are some bacteria which are responsible for locculating protein production. Bacillus subtilis and Alcaligenes latus are the bacterial species which secrete bioflocculant made up of polysaccharides only while Arcuadendron sp. and Arathrobacter sp. secrete glycoprotein bioflocculant (Abu et al. 2018). Kurane et al. (1994) reported that Rhodocccus erythropolis were capable of bioflocculant production, but loses the flocculation function while enzymatic degradation (Subudhi et al. 2015). The mechanism followed

by flocculation is based on adsorption. It helps in the formation of metalfloc interaction, in which the formation of floc is dependent on the ionic groups of bioflocculant such as carboxyl and amino group. The interaction between metal bindings is influenced by the characteristics of heavy metals like Physio-chemical interaction, ionic strength and flow tertiary structure. However, the roles of bioflocculant have yet not been reported for the detoxification of mercury.

Detoxification by fungi: Fungi have been broadly used to remediate soil and waste water as it is recognized and received huge attention in the direction of remediation of a heavy metal contaminated environment as an adsorbent and bioacumulator. The method of metal detoxification in fungi is a complex process which depends on the quality, biomass type, metal chemistry and environmental variables. Its ubiquitous nature and dominant presence diverted a lot of attention towards the use of live or dead fungal biomass for the detoxification of heavy metals (Gururajan and Belur 2018). The fungal community has a higher proportion of cell wall material which enhance the functional group for metal binding and metal sequestration capability of the fungi (Svecova et al. 2006). An alive, dead, immobilized and pre-treated form of Aspergillus sp, Trichoderma sp, Penicillium sp, Botrytis sp, Neurospora Sep, Saprolegnia sp, separated from diverse environmental areas have been used for removal of toxic contaminants with appreciable results (Gururajan and Belur 2018). Also the physicochemical interaction with the cell surface and the available functional group helps in the sorption of heavy metal by cell wall of fungi. In several experiments, it is proved that biosorption and bioaccumulation achieved massive attention for remediation than biotransformation as these are the most efficient mechanism of remediation. For example, Kurniati (2013) isolated Aspergillus flavus strain KRP1 from tropical forest soil and this fungal strain showed the best growth in 25ppm of mercury while the minimum inhibitory concentration (MIC) to mercury was at 100ppm. Aspergillus flavus was apt to remove 97.50% and 98.73% mercury from static and shaken systems respectively. Hence, Aspergillus flavus strain KRP1 sounds to have the possible capability to remediation of mercury through the mechanism of biosorption. Gurujan et al. (2018) isolated 4 fungal isolates resistant to heavy metal from a scrap dumpsite. The Minimum inhibitory concentrations of these 4 fungal isolate were 10-100 mg/l for mercury (II), 50-400 mg/l for lead (II), 50-400 mg/l for cadmium, and 10-100 mg/l for arsenic (III). The isolated strain was efficient for lead (II) removal about 95%. Very scant removal capability was found in the case of cadmium and mercury by all the 4 fungal isolates by about 10-20%. In the case of arsenic, a total of 58.8% removal was observed by all the fungal isolates. Hindersah et al. (2018) studied the tolerance of fungal growth in the presence of mercury. He isolated four fungal isolates from the Wamsait village in Buru Island. The A and C isolates were from the water Spinach (Ipomoea reptans) and B and D were from the Wiregrass (Eleusine indica L. Gaertn) rhizospheres. All the four isolates were exhibited resistance to 25 mg/kg of mercury and the two fungal species Aspergillus Niger (A) and Aspergillus flavors (B) were found to be enhanced the soil's availability of Hg and by this experiment he suggested that indigenous Hg resistant fungi able to mobilize mercury in the soil and deliver as potential bioremediation agent for mercury-contaminated soil. Hadiani et al. (2018) investigated the biosorption potential of Saccharomyces cerevisiae in aqueous solution. The optimal conditions for Hg biosorption were 5.47 pH, 79.8 µg/l initial Hg2+ concentration and biomass 47.7×107 CFU respectively. The results showed the removal efficiency of 88.9% under optimal condition and this finding suggest that Saccharomyces cerevisiae have the ability to remove and mitigate precarious elements even at very low concentration. Hoque and Fritscher (2016) reported the unique ability of Mucor hiemalis that can convert the highly toxic ionic mercury into elemental mercury by intracellular accumulation. Mucor hiemalis was isolated from microbial biofilm grown in Marching spring water (source of mercury), Germany. This fungus has the ability to remove about 99% mercury from the aqueous medium within 10-48 hours and proved as first eukaryotic microbe that is able to survive under sulfur reducing condition at low temperature with potential application in remediation of mercury pollution. Some Fungal biosorption is summarized in the Table 5.

SI BO.	Name of fungi	Isolation site	Optimum (pH & Temperature	Remediation %	Tolerance (mg1)	Time	References
1	Rhitopus stolonjier	Dumpsite (Industrial area)	4 & 37*C	98%	100	24 h	Abdoun-Ouallouche et al. 2014
2	Aspergillus flovas	Forest soil (Mercury-contaminated)	6-7 & 37*C	97%	100	72 h	Kumiati et al. 2014
3	Saccharowyces cerevisiae	Research laboratory	5-6 & 25-35 °C	93.4%	52.4	72 h	Hadian et al. 2018
4	Aspergilles, Cladosportem, Trichoderma, Alternaria genera	Mercury mining area (Rudiany in central Slovakia)	4.5-5.3 & 25°C	80%	32.7	7 days	Unik et al. 2014
5	Gracilaria corticata,	Persian Gulf on Queshm Island	5 & 25°C	92.5%	200	90 min	Esmaeili et al.2015
6	Sargazzan glaucezona	Persian Gulf on Queshm	7 & 25°C	97.3%	1000	30 min	Esmaelli et al. 2015

Detoxification by Algae: Algae is eukaryotes, natural, consist of chlorophyll renewable biosorbent, ubiquitous in nature extensively used for the sequestration of heavy metals pollution. The constitutive mechanism of biosorption shown by the different type of algae helps in the sequestration of heavy metal contamination. High efficiency, easy to handle, economical, huge availability and high binding affinity of algae made it universal bio sorbent for heavy metals detoxification (Zeraatkar et al. 2016). The heavy metal biosorption by algae mainly depends on factors like pH, temperature, metal ion concentration, the biomass of algae and the presence of other competing ions. The distribution of biomolecules such as lipids, protein, and carbohydrates in the cell wall of algae help in reaction with the heavy metals. These biomolecules consist of functional groups includes the oxygen, nitrogen of the peptide bond, histidine group, amino, phosphate, carboxyl, ether, imidazole, thiol, phenolic, sulfhydryl, hydroxyl, sulfate, phosphoryl, phosphate and amide moieties usually found in the cytoplasm, at the cell wall, and vacuoles and these groups are authoritative for the coordinating bond formation with the metallic ions, also promote the metal ion adsorption in an algal cell. The variation of the adsorption capability of different algal strains could be due to a variety of distribution and abundance of algal cell wall composition (Polysaccharides and proteins). Cain et al. (2008) assessed the absorption of mercury by two cyanobacterial strains Spirulina platensis and Aphanothece flocculosa and these strains were able to remove 98% of the mercury with a primary of 10 ppm of mercury concentration at pH 6 for both the strains. The existence of dissolved iron, nickel and cobalt cation were found to initiated a coactive role for Hg2+ uptake by both strains. Plaza et al. (2011) studied the absorption ability of two brown algae belonging to the Laminariales order and Phaeophyta class i.e Macrocystis pyrifera and Undaria pinnatifida. As compared to Macrocystis pyrifera(2.7L/mmol), Undaria pinnatifida(4.4 L/mmol) showed greater absorption affinity for mercury uptake while in the presence of other opponent heavy metals such as Cd (II), Ni (II), and Zn (II) the mercury uptake was notably decreased. This study concluded that Hg (II) can bind with S=O (sulfonate) and N-H (amine) functional groups through Fourier transform infrared spectrometry analysis and Macrocystis pyrifera and Undaria pinnatifida proved to be the best algae in remediation of mercury. The biosorption ability of different algae is shown in Table 6.

Sl no.	Name of algae	Isolation site	Mechanism used	Optimum (pH & Temperature	Percentage remediation	Time	References
1	Cladophora fasicularis	Okha Port, Northwest coast of India	Biosoption	NA	95.67%	120 min	Kumar et al. 2009
2	Chlamydomonas reinhardtii	Kızılırmak River in Turkey	Biosoption	6 & 35 °C	72.2%	60 min	Tüzün et al. 2005
3	Cystosetra baccata	Coasts of A Coruña (Galicia, NW Spain)	Biosoption	4.5 & 22 °C	80%	100 min	Herrero et al. 2003
4	Cladophora sp.	AlexandraDam, Springs,Johannesburg, Gauteng, SouthAfrica	Biosoption	5 & 16°C	\$7.11%	60 min	Mokone et al. 201
5	Nostoc paludosum	Gold processing plant, NovaLima	Bioaccumulation	7 & 20°C	96%	96 h	Franco et al. 2018
6	Cystoseira myricaas	Persian Gulf, Bushehr city	Biosoption	3 & 45°C	95%	NA	Zarei et al. 2017
7	Chlorella Vulgaris	Purchased from Qeshm	Biosoption	NA & 21°C	85.88%	24 h	Fard et al 2017

Phytoremediation of mercury: The removal, segregation or sequestration of toxic metals from the contaminated or polluted environment with the help of living green plants is known as phytoremediation, also botanoremediation, agroremediation, green remediation and vegetative remediation (Xun et al. 2018). The mechanism like phytofiltration, phytostabilization, phytovolatilization and phytoextraction of plants make them a chief biotic factor in Hg cycle. Different plants show unimaginable tolerance for heavy metals like Hg, Pb, Cd, As, Cr, Cu, Al, etc. Having the competency to take in heavy metals from the contaminated soil and waste water, plants accumulate heavy metals and deposited them in tissues. The organic and inorganic compound of mercury is assimilated by the plant through root systems, directly through leaf absorption or by stomata (Fernández-Martínez et al. 2008). Plants usually accumulate heavy metals in the root and often in the shoot of the plant by translocation. A lot of studies, experiments and field trials has been successfully performed and proved phytoremediation is an auspicious technology and less costly than physical and chemical methods for the remediation of mercury pollution on the contaminated soil and waste water. Accumulator plants have the ability to concentrate heavy metals as well as secure its delicate structure and cellular or biological activity from a disproportionate amount of heavy metals, especially in the case of mercury which is highly toxic even at low concentration. It is an obvious fact that the heavy metals cause detrimental effects on the plants and animal due to interaction with the biological cells and coaction with the active sites of molecules leads the reciprocal action, such as inactivation of protein, enzymes and functional groups as well as oxidative damage generated by the reactive oxygen species (ROS) (Hossain et al., 2012). By the same way, mercury also causes dwindle biomass and plant growth due to arrest cell division and deluge of ROS e.g. Superoxide anion radical (O2), H2O2, hydroxyl radical (OH•), and lipid peroxides in plants. Mercury is a strong genotoxic as well as phytotoxic metal. Plant cells have antioxidants like l-glutathione, ascorbate and tocopherol, and antioxidative enzymes: ascorbate peroxidase (APX), superoxide dismutase (SOD), glutathione reductase (GR), and catalase (CAT) that engage in scavenging active oxygen species such as 1O2, O2-, H2O2 and hydroxyl radical (OH•) (Ishar and sahi 2006; Belzile et al. 2006). The metal-chelating compound synthesized by plants (phytochelatins), mammals (metallothioneins), fungi and algae also act as a defense mechanism against heavy metals. Phytochelatins are thiol-rich proteins found in plants helps in minimizing the stress caused by heavy metals in a living organism (Gómez-Jacinto et al. 2015). Xun et al. (2017) was screened out Cyrtomium macrophyllum is a potential mercury accumulator plant. While pot experiment Cyrtomium macrophyllum showed accumulation of 36.44 mg/kg of mercury in its aerial parts with a translocation factor of 2.62, showed maximum tolerance of 500 mg/kg in the soil. Because of enhanced superoxide dismutase activity and glutathione, and proline accumulation induced by mercury stress, the leaf tissue also demonstrated big resistance towards mercury stress, which later induce the mercury translocation to its aerial portion from the roots and hence Cyrtomium macrophyllum act as a favorable plant for the remediation of mercury-contamination. Liu et al. (2017) determine the absorption capacity of herb species like Opuntia stricta, Oxalis corniculata, Aloe Vera, Chlorophytum comosum and Setcreasea purpurea in different concentration of mercury solution. By comparing the deposition rate of mercury in root and shoot of the herb species in different concentration, he found that the accumulation ability of root was greater than the shoot of herb species. Among all, Oxalis corniculata was the most promising for translocation of Hg and advisable for remediation of the mercury-contaminated site having a concentration less than 500g/l respectively. Skinner et al. (2007) performed an experimentation to assess the remediation potential of hydrophytes. The hydrophytes were zebra rush (Scirpustaberna emontani), taro (Colocasia esculenta), water lettuce (Pistia stratiotes), and water hyacinth (Eichornia crassipes). Among all aquatic plants, Water lettuce and water hyacinth were showed more efficient in mercury uptake via root and shoots accumulation followed by Taro and Zebra rush. These aquatic plants were placed in different concentration of mercury, i.e. 0 mg/L, 0.5 mg/L and 2 mg/L for 30 days and showed the good accumulator of heavy metals especially for mercury in aquatic ecosystems and help in phytoremediation.

Conclusion

Mercury pollution has been a global issue for the natural ecosystem and human health and it is necessary to decontaminate the environment from the heavy metals which are highly essential for the goodwill of a healthy environment. For the environmental cleanup, the remedial method for heavy metals contamination from soil and waste water should be based on inventive sustainable technologies. In a sustainable approach, an absorption, bioaccumulation and biotransformation mechanism have been proven as potential, innovative and worthwhile approach for remediation of an Hgcontaminated soil and waste water. Bacteria, fungi and algae have tremendous metal uptake ability, facile availability, and high biomass generation scope makes them efficient in remediation as well as proved that they can be the superior agent for the remediation of mercury. The role of mercury reductase enzyme in remediation help in better perceptive of mercury removal mechanism, also help in improving the current technologies. The use of exopolysaccharides in heavy metals detoxification also facilitates the greener technology for removal. Now these days biotechnological approaches and tools are also implemented in the remediation of heavy metals which might be used for enhancing the resistance and tolerance potential of microbial strains towards heavy metals. Undoubtedly the biological method of remediation is the most considerable and impressive method without any ruinous impact on the ecosystem. Therefore, remediation of mercury with the help of a biological method is great effort for removal from the environment with fewer side effects.

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